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Surface Modification of Pd/α-Si_3N_4 Catalysts Through the Solvent Used During Synthesis. Implications on the CO Chemisorption Properties and Catalytic Performances

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Abstract Palladium catalysts supported on α-Si_3N_4 were prepared by impregnation with Pd(II)-acetate dissolved either in toluene or in water. The mean metal particle size of ~0.5 wt% Pd catalysts was similar (~5 nm) and independent of the way of preparation. Nevertheless, the two catalysts present very different chemisorption behaviour chemisorptive and catalytic properties. Fourier transformed infrared (FTIR) spectra of adsorbed CO at different temperatures (ranging from room temperature to 300 °C) show a very different behaviour for both catalysts. While the CO adsorption states on the Pd/α-Si_3N_4 prepared in toluene are very similar to those generally measured for silica and/or alumina supported palladium catalysts, CO chemisorbs less strongly on Pd/α-Si_3N_4 prepared in water and on different adsorption sites. The Pd/α-Si_3N_4 catalyst obtained by aqueous impregnation is much less efficient for the methane total oxidation. It is less active and less stable: it deactivates strongly after 3 h on stream at 650 °C. The two catalysts present about the same activity for the 1,3-butadiene hydrogenation after stabilisation at 20 °C. But, the catalyst prepared in water shows a much better selectivity to butenes. The results are discussed in terms of the possible migration of silicon atoms from the silicon nitride support to the surface of the palladium particles, when the catalyst is prepared in water. This is not the case when prepared in an organic solvent.

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1 Introduction

Catalytic combustion of methane and partial hydrogenation of butadiene are considered as test reactions for palladium supported catalysts; they are carried out respectively at high and low temperature, and in oxidizing and reducing environments. Moreover, they are both of great industrial importance.

Catalytic combustion of methane can be applied in many domestic and/or industrial fields [1]. It is a way to produce heat and infrared emission without nitric oxides emissions. Nitric oxides (NO*x*) are formed by oxidation of atmospheric nitrogen or by oxidation of the nitrogen compounds contained in the fuels at high temperatures. Thus hot spots need to be avoided. Pd, in its oxidized state, is known to be a very active catalyst for this reaction [2]. But, the deactivation of catalysts is an important issue for the design of a commercial catalytic system for such a high temperature reaction. Poisoning, sintering, coking or fouling are reported as causes of the catalyst deactivation [3–6].

Partial hydrogenation of dienes (and alkynes) is a way to eliminate 1,3-butadiene (or acetylene) present as an impurity in C_4 alkenes (or ethylene) [7, 8]. An efficient process will consequently work in such a way that the complete hydrogenation of butadiene into butenes (or acetylene into ethylene) will be effective until the complete conversion of the diene (or acetylene) is reached, i.e. avoiding any formation of the completely hydrogenated (butane or ethane) molecules. For this reaction, Pd is still considered the best catalyst. However it was shown that its

activity and selectivity can be strongly influenced by the metal dispersion, the nature of the support and the preparation method [9–11]. Moreover, it is known that the presence of additives can modify strongly the properties of Pd catalysts for this reaction [7, 12, 13].

Silicon nitride is a thermostable material, having a very high thermal conductivity. It was shown that it can be used as support for metallic particles, giving rise to highly efficient catalysts in comparison with metals supported on oxides for oxidation reactions working at high temperatures [14–16]. For example, Pd/α-Si_3N_4 catalysts prepared by decomposition of Pd-acetyl-acetonate dissolved in toluene are very efficient for methane combustion [14]. Moreover, they present similar properties to that of Pd supported on more classical (silica, alumina) oxide supports for the gas phase 1,3-butadiene hydrogenation reaction, both with respect to their activity and selectivity to butenes [17]. Nevertheless the use of water as solvent is preferred over toluene for catalyst preparation at industrial levels due to environmental and health issues.

In this paper we present results on the influence of the solvent (toluene and water) used during the preparation of α-Si_3N_4 supported Pd (from Pd-acetate precursor) catalysts with respect to CO adsorption and the catalytic performance for the methane total oxidation and for the 1,3-butadiene hydrogenation reactions.

Transmission electron microscopy (TEM) and x-ray photoemission spectroscopy (XPS) were used to characterise the morphology and the electronic properties of the Pd particles, CO chemisorption is investigated by vibration spectroscopy.

2 Experimental

2.1 Catalyst Preparation

The silicon nitride support, approximately 7 m^2/g BET specific surface area, was provided by Goodfellow. It is mainly constituted the low temperature hexagonal α-phase; although the presence of the high temperature β-phase was also observed by XRD [14].

Catalysts were prepared by impregnation of the as-supplied support with the adequate amount of Pd(II)-acetate [$Pd(CH_3CO_2)_2$] (98% from STREM) dissolved either in toluene or in water. After evaporation of the solvent and drying at 80 °C or 100 °C for toluene and water respectively, the catalyst precursor was decomposed under an argon flow at 500 °C during 2 h with a heating rate of 1 °C min^{-1} and cooled to room temperature (RT) under this neutral atmosphere. It was then calcined during 2 h at 350 °C under oxygen flow (heating rate of 1 °C min^{-1}) and further reduced under hydrogen flow during 2 h at 500 °C (heating rate of 1 °C min^{-1}). Finally, the reduced catalysts after cooling to RT were kept under a flow of Ar for half an hour.

2.2 Catalyst Characterisation

Induced Coupled Plasma (ICP) chemical analysis was used to determine the metal content of the catalysts. The samples were put in acid solutions and heated. The acid solutions used were either $H_2SO_4/HNO_3/HF$ at 250 °C or $HF + (2/3)HCL/(1/3)HNO_3$ at 150–200 °C. The acid attack does not dissolve completely the silicon nitride and a grey residue was observed. This does not affect the interpretation of the chemical analysis since in both cases (catalysts prepared in water and in toluene) the amount of silicon nitride that is not dissolved is about the same and it is negligible (<<1%). The solutions were filtered before analysis by optical ICP in a SPECTRO monochromatic spectrophotometer (Pd wavelength was 340.6 nm).

The catalysts morphology (size and distribution of the Pd particles supported on the powders) was determined by transmission electron microscopy (TEM). The microscope is a JEOL JEM 2010, operating at 200 kV, equipped with a LaB_6 tip, a high resolution pole-piece (point resolution: 0.196 nm) and a Pentafet-LinK ISIS EDS-X spectrometer (Oxford Instruments). Size distributions were obtained from TEM micrographs; the mean sizes of the particles (d_{Pd}) are determined using the formula $d_{Pd}(nm) = \Sigma n_i d_i / \Sigma n_i$, where n_i is the number of particles corresponding to a diameter d_i (nm).

Binding energies of the Pd-3d electronic levels were determined from XPS measurements performed with a Fison Instruments ESCALAB 200R machine. Since some charge effects appeared during measurements all the data are corrected by taking the XPS binding energy (BE) of the N_{1s} level of Si_3N_4 at 397.6 eV as reference energy [18].

2.3 CO Chemisorption and IR Measurements

Infrared spectra were collected with a FTIR Brucker spectrometer (model Vector 22) equipped with a DTGS detector using an IR cell with CaF_2 windows. Samples were shaped by pressing 10 mg of catalyst into a disc of 18 mm in diameter. Each spectrum corresponds to 400 scans at 2 cm^{-1} resolution; requiring a data acquisition time for one spectrum of one minute.

The catalysts were pre-treated under oxygen flow at 500 °C and reduced under hydrogen at 350 °C before exposure to carbon monoxide (CO) at room temperature (RT). IR spectra were then recorded after removing gaseous CO by evacuation (30 min) at RT, and after heating the samples at respectively 100 °C, 200 °C and 300 °C under vacuum conditions.

2.4 Catalytic Measurements

The total oxidation of methane reaction was performed between 25 °C and 650 °C in a flow tubular quartz reactor. A 0.2 g mass loading of catalyst was used for each experiment. The catalytic bed, located in the middle of the furnace (30 cm length), measured about 2 mm in length. The temperature of the catalyst was measured with a thermocouple having its tip located in the catalytic bed. The flow of reactants (methane, oxygen and nitrogen in ratio 2.5/19.5/78) was set at 100 mL/min. The products were analyzed by mass-spectrometry. CO_2 and H_2O were the only products detected. Methane conversion versus temperature was measured for the fresh catalysts and after a first reaction cycle followed by 3 h operating at 650 °C.

The 1,3-butadiene hydrogenation was carried out at 20 °C in a flow reactor at atmospheric pressure. In order to improve the heat transfers between the thermostatic bath (which determines the reaction temperature) and the catalyst, metallic stainless steel tubes of 1/4″/1/6″ outer/inner diameter were used as reactors. 5 mg of catalyst was blended with 45 mg of the α-Si_3N_4 inert support before introduction in the reactor.

As prepared catalysts were pretreated in the reactor during 2 h at 500 °C in flowing O_2 and then reduced in H_2 during 1.5 h at 350 °C. They were cooled under a He flow before the catalytic studies.

The reaction was performed in excess of hydrogen (H_2/HC = 10), the reactive mixture being diluted in He (He/(H_2 + HC) = 6). The relative flows were set with Brooks flow-meters; the total flow was fixed at 10.8 L h^{-1}. Products analysis was performed by gas chromatography. The selectivity into butenes is defined by $S_1 = P_{butenes}/\Sigma\ (P_{butenes} + P_{butane})$; the relative amount of 1-butene in the butenes cut is measured by $S_2 = P_{1\text{-butene}}/\Sigma(P_{butenes})$. For the turnover frequency (TOF) determination, the dispersion D is calculated by the expression D = 1.1/d (d being the mean size diameter, expressed in nm), valid for fcc Pd particles [19].

3 Results and Discussion

The Pd content determined by ICP was respectively 0.58 wt% for the catalyst prepared in toluene and 0.53 wt% for the catalyst prepared in water. These catalysts will be referred to hereafter as Pd/α-Si_3N_4-tol and Pd/α-Si_3N_4-wat respectively.

3.1 Catalyst Characterisation by TEM and XPS

Representative TEM micrographs of the studied catalysts are given in Fig. 1, together with the size distributions. The mean particle size of the Pd is close to 5 nm whatever the preparation method (see Table 1).

XPS experiments evidenced only a small difference in the Pd-3d binding energies (BE) for both catalysts (see Table 1). However, the BE value of the Pd-$3d_{5/2}$ is notably higher than the one measured for a Pd/SiO_2 catalyst with Pd particles of about the same size, i.e. 334.9 eV [17]. SiO_2 is often considered as a "neutral" support with respect to a metal-support interaction. In a simplified manner, one can therefore consider that Pd is in a neutral state on SiO_2 but somewhat electron deficient on α-Si_3N_4, i.e. a peculiar metal-support interaction does exist for the Pd/Si_3N_4 catalysts.

3.2 IR of CO Adsorbed as a Probe

The infrared spectra of carbon monoxide irreversibly adsorbed at RT, 100 °C, 200 °C and 300 °C over the Pd/α-Si_3N_4-tol are given in Fig. 2a. In the spectrum obtained at RT bands corresponding to the ν_{CO} stretching modes at 2,075, 1,970, $\approx$1,920 and $\approx$1,830 cm^{-1} can be identified. Such a spectrum is very similar to those obtained for CO adsorbed on Pd/SiO_2 [20], Pd/Al_2O_3 [21] and on a model catalyst made of small particles deposited on an oxidised NiAl(110) single crystal [22]. With increasing temperature, the global intensity of the IR bands decreases; no CO ad-species remain on the Pd particles after evacuation at 300 °C. It is clear that some specific states of adsorbed CO desorb at a lower temperature. As a matter of fact, only vibration modes at 1,910 and 1,830 cm^{-1} are still observed after evacuation at 200 °C. It is a priori difficult to identify un-ambiguously the different adsorption sites. However, on the basis of previous results obtained for CO chemisorbed either on supported particles or on single-crystal Pd surfaces one can make some suggestions to interpret the present data. One can propose that CO adsorbs on Pd in four modes, depending on both the site for adsorption and the CO–CO interactions: they would correspond to linear (around 2,075 cm^{-1}), compressed-bridged (around 1,970 cm^{-1}), isolated bridged (nearby 1,920–1,910 cm^{-1}) and tri-coordinated ($\approx$1,830 cm^{-1}) bonds [13, 23]. It is also tempting to interpret the spectra in terms of CO adsorbed on the different facets and/or on the edges present on the Pd particles, as proposed by Freund et al. [22]. Actually, in their more stable state Pd supported particles present mainly (111) and (100) facets [22, 24]. It has been shown that CO chemisorbs more strongly on Pd(100) than on Pd(111), with initial isosteric heats of adsorpion of respectively 38 and 30 kcal mol^{-1} [25]. Moreover, on the basis of the coverage dependence of the ν_{CO} vibration modes for CO adsorbed on Pd(100) [25] and Pd(111) [26] the spectra can be tentatively interpreted as follows.

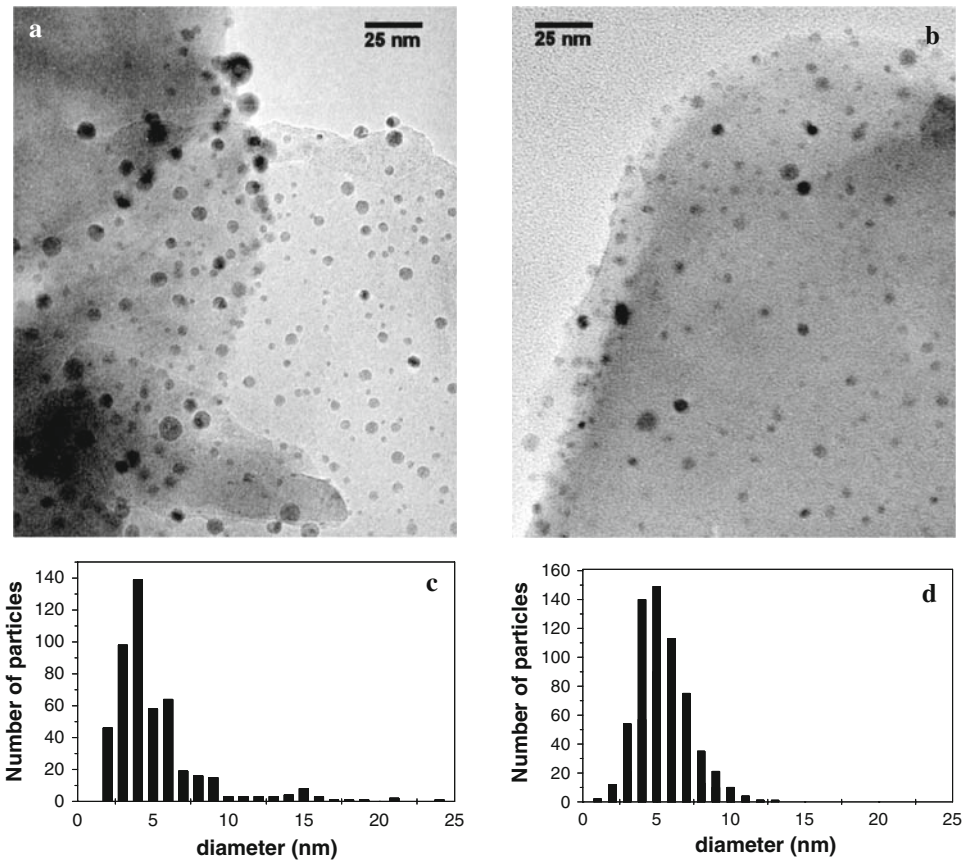

Fig. 1 Transmission electron micrographs of the two catalysts (**a**, **b**) and respective size histograms (**c**, **d**). **a**, **c** Pd/α-Si_3N_4-wat. **b**, **d** Pd/α-Si_3N_4-tol

Table 1 Pd weight %, mean particle size and Pd-$3d_{5/2}$ XPS binding energy measured for the Pd/α-Si_3N_4-tol and Pd/α-Si_3N_4-wat catalysts

	Pd wt% (from ICP)	TEM mean particle size (nm)	XPS Pd-$3d_{5/2}$ BE (ev)
Pd/α-Si_3N_4-tol	0.58 wt%	5	335.6
Pd/α-Si_3N_4-wat	0.53 wt%	4.9	335.8

At high CO coverage (see Fig. 2a at RT):

- 2,075 cm^{-1}: linear CO, on (111) facets,
- 1,970 cm^{-1}: compressed-bridge CO, on (100) facets,
- 1,920 cm^{-1}: bridge CO, on (111) facets,
- 1,830 cm^{-1}: tri-coordinated CO, on (111) facets.

As the sample temperature is increased, i.e. as the CO coverage is decreased, there is, firstly, desorption of linear and bridge bonded CO ad-species located on the (111) facets. Simultaneously, the compressed-bridge CO species present on the (100) facets transform into bridge bonded CO (without CO–CO interactions), inducing a shift of the ν_{CO} stretching vibration from 1,970 to 1,910 cm^{-1}. Some tri-coordinated CO species are also still present on the (111) facets (see Fig. 2a, at 200 °C). One can think that there are not enough CO species adsorbed on the edge atoms of the rather big (5 nm mean diameter) particles studied in the present work to allow their possible observation by IR spectroscopy. If such CO ad-species actually exist they would be in a linear configuration, but with a stronger bond than on higher coordinated surface sites present on the facets [24]. Consequently, they would be desorbed after the CO species located on the facets, and should be still visible in the spectra recorded at high temperature, which is not the case.

The infrared spectra of carbon monoxide irreversibly adsorbed at RT, 100 °C and 200 °C over the Pd/α-Si_3N_4-wat are shown in Fig. 2b. The intensities of all the bands is much lower than for CO adsorbed on the Pd/α-Si_3N_4-tol catalyst (Fig. 2a). Moreover, no adsorbed CO species remain on the Pd metallic particles at 200 °C. It can be stated that CO is less strongly adsorbed over the Pd/α-Si_3N_4-wat catalyst than over the Pd/α-Si_3N_4-tol catalyst.

In the spectrum obtained at RT, one can identify bands corresponding to ν_{CO} stretching modes at 2,065, 1,965 and 1,910 cm^{-1}. Their intensity decreases with increasing temperature without any significant energy shift. This indicates a lack of CO–CO interactions, which can be the consequence of geometric dilution effect induced by the presence of inactive elements at the surface of the metal particles. This is strongly supported by the comparison of FTIR spectra of CO adsorbed on the Pd/α-Si_3N_4-wat catalyst with those obtained by Shin et al. over Si-modified Pd

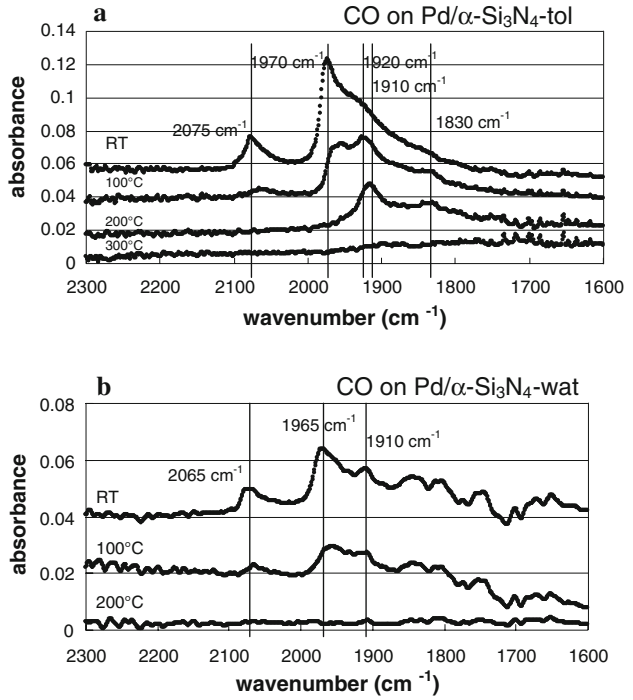

Fig. 2 Infrared absorption spectra of CO irreversibly adsorbed on the Pd/α-Si_3N_4-tol catalyst (**a**) and on the Pd/α-Si_3N_4-wat catalyst (**b**), after removing gaseous CO by evacuation at room temperature (RT), 100 °C, 200 °C and 300 °C respectively. The spectra have been shifted for clarity

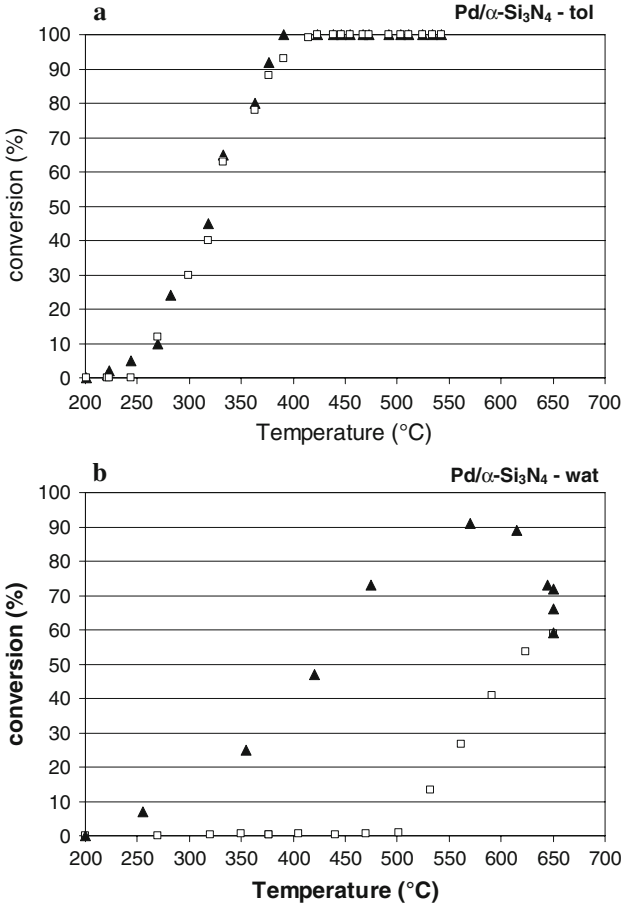

Fig. 3 Conversion of methane in the reaction of total oxidation of methane (CH_4 (2.5%), O_2 (19.5%), N_2 (78%); 100 mL/min) as a function of temperature for the fresh catalysts (▲) and the catalysts having worked for 3 h at 650 °C in reaction conditions (□) showing a deactivation of the Pd/α-Si_3N_4-wat catalyst (**b**) compared to the Pd/α-Si_3N_4-tol one (**a**)

catalysts [13, 27]. One can therefore soundly propose that the change of the CO chemisorption characteristics observed for the Pd/α-Si_3N_4-wat catalyst is the consequence of the presence of Si ad-atoms at the surface of the Pd particles that block adsorption sites otherwise available on the Pd/α-Si_3N_4-tol catalyst.

3.3 Methane Total Oxidation

The catalyst prepared in toluene was the most active. The total conversion of methane under the experimental conditions was achieved already at 400 °C (Fig. 3a) and the temperature at which 50% conversion occurs (320 °C) is close to that of the Pd/α-Si_3N_4 sample prepared with Pd-bis-acetylacetonate in toluene [14]. The catalyst remains active and stable after 3 h of time on stream at 650 °C (Fig. 3a). Conversely, the Pd/α-Si_3N_4 catalyst obtained by aqueous impregnation is less active and less stable. Total conversion of methane was never reached and the catalyst deactivates during the first cycle of reaction (Fig. 3b). The catalytic behaviour is very different despite an initial similar average Pd particle size and the dispersion of the active phase observed by TEM for both catalysts (Fig. 1 and Table 1). TEM observations made after reaction showed that some sintering of the Pd particles occured during reaction; being a little bit more severe for the catalyst prepared in water. Actually, the mean diameter of the Pd particles was measured as 6.0 nm for the Pd/α-Si_3N_4-tol catalyst and 8.3 nm for the Pd/α-Si_3N_4-wat catalyst. The difference in the increase of size, and the consequent decrease of available active sites, cannot explain the observed loss in activity [28, 29]. Based on the CO chemisorption results, one can propose that some Si ad-atoms present on the Pd particles just after the preparation can be oxidized generating some coating of the metal particles. However, TEM observations did not reveal such phenomenon, as it was the case for sub-nanometer layers formed after methane oxidation on Pd/β-Si_3N_4 [6] and on Pd/α-SiC [5] catalysts. This clearly indicates that, in the present case, Pd surface coating is certainly on the sub-monolayer range and localised on specific sites, which renders its direct observation difficult with the physical methods of characterisation used.

3.4 1,3-butadiene Hydrogenation

In Fig. 4a and b are reported the conversion, the S_1 selectivity into butenes and the S_2 selectivity of 1-butene versus time for the two studied catalysts at 20 °C.

The Pd/α-Si_3N_4-tol catalyst shows a stable activity. The conversion is close to 30% after 14 h time on stream. This corresponds to a turnover frequency (TOF) of 8 s^{-1} per Pd surface atom, for the experimental conditions used. The S_1 selectivity into butenes is low (≈50%) (Fig. 4a). The S_2 selectivity, which measures the fraction of 1-butene among the all the (1- + 2-) butenes, amounts to 30%. The values of S_1 and S_2 are quite comparable to those measured for other Pd catalysts on various supports under the same experimental conditions, at comparable values of the conversion [17].

The behaviour of the Pd/α-Si_3N_4-wat catalyst is somewhat different. It first deactivates notably with time; while simultaneously the S_1 selectivity slightly increases. After 14 h of operation, the conversion is nearly 40% (TOF ≈11 s^{-1}) and the S_1 selectivity is close to 90% (Fig. 4b). S_2 amounts to ≈40%.

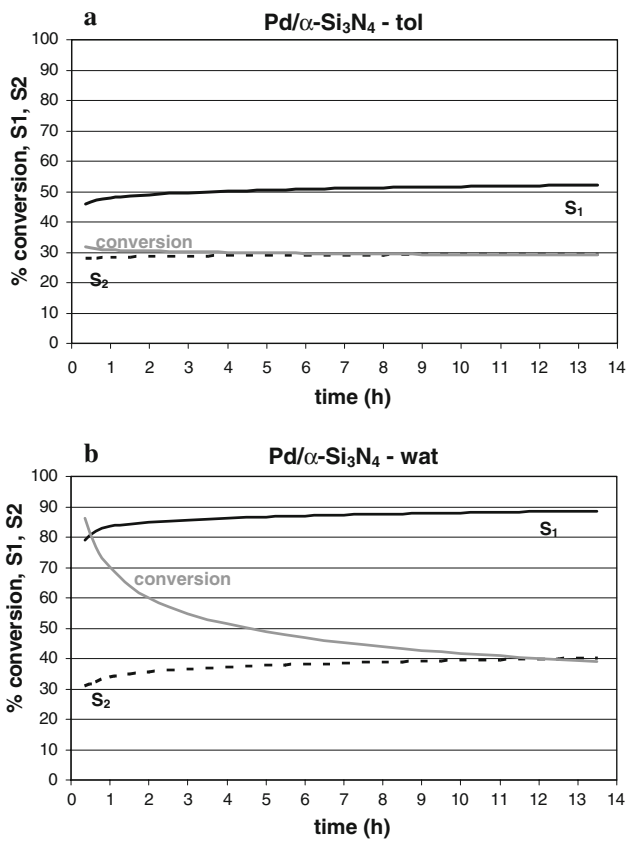

Fig. 4 1,3-butadiene conversion (%), selectivity $S_1 = P_{butenes}/\Sigma (P_{butenes} + P_{butane})$ (%) and selectivity $S_2 = P_{1\text{-}butene}/\Sigma(P_{butenes})$ (%) versus time for the Pd/α-Si_3N_4-tol catalyst (**a**) and for the Pd/α-Si_3N_4-wat catalyst (**b**). Temperature: 20 °C. Flow rates: H_2 = 1.4 L h^{-1}, butadiene = 0.14 L h^{-1}, He = 9.3 L h^{-1} (i.e. 129 mbar H_2, 13 mbar butadiene and 858 mbar He)

The main conclusion is that the Pd/α-Si_3N_4 catalyst prepared in water is much more selective into butenes than the catalyst prepared in toluene, when compared at similar conversion levels. An increase of the selectivity of the Pd particles in this reaction is often the consequence of foreign elements present at the surface of the Pd [7, 12]. Among them, it has been shown that silicon ad-atoms modify Pd catalysts that then show higher selectivity towards ethylene for the selective hydrogenation of acetylene together with producing less amount of green oil [13, 27, 30]. The preparation in water, used as solvent of the palladium precursor, undoubtedly induces a chemical reaction with the silicon nitride support, generating diffusion of some Si atoms towards the Pd metal particles. This is consistent with the data issued from the vibrational spectroscopy of CO adsorbed on the Pd/α-Si_3N_4-wat catalyst that could be explained by a dilution effect by an inactive species (Si) at the surface of the Pd particles. Actually, it is stated that better selectivities for many selective hydrogenations can be obtained by partial poisoning [31]; the selectivity into butenes (or ethylene) can be notably improved when the catalyst surface is modified by additives [7, 12], inducing a geometric "dilution" effect, which reduces the available number of multiple metallic surface sites. An electronic effect that modifies the adsorption strength between the reactants and the active metal surface atoms, can also be considered. Silicon at the surface can act in such a way [13].

4 Conclusions

The chemical properties of Pd supported on α-Si_3N_4 catalysts strongly depend upon the preparation process. Catalyst prepared from Pd-acetate, as the metal precursor, dissolved in toluene and in water show very different chemical properties with respect to CO chemisorption and modified catalytic performances for both the methane total oxidation and the 1,3-butadiene hydrogenation reaction. Carbon monoxide chemisorbs less strongly on the Pd/α-Si_3N_4 catalyst issued from Pd-acetate dissolved in water. It deactivates during methane combustion, while the one prepared in toluene remains very stable. With respect to the gas phase 1,3-butadiene hydrogenation reaction, the Pd/α-Si_3N_4-wat catalyst produces less butane, i.e. it is more selective to butenes.

The results obtained for the Pd/α-Si_3N_4-wat catalyst can be tentatively interpreted in terms of the presence of silicon atoms migrating from the support to the surface of the Pd metal particles in the presence of water during the

preparation process leading to a modification of the chemisorption and catalytic properties. This is not the case for organic solvents.

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